



Attorney's Docket No. 9362-4

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PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re: Williams *et al.*  
Serial No.: 10/662,621  
Filed: September 15, 2003

Group Art Unit: 1615  
Confirmation No.: 9764  
Examiner: Levy, Neil S.

For: **CARBON DIOXIDE-ASSISTED METHODS OF PROVIDING  
BIOCOMPATIBLE INTRALUMINAL PROSTHESES**

Date: July 24, 2007

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Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1450

**APPELLANT'S BRIEF ON APPEAL UNDER 37 C.F.R. § 41.37**

Sir:

This Appeal Brief is filed pursuant to the "Notice of Appeal to the Board of Patent Appeals and Interferences" filed May 24, 2007.

It is not believed that an extension of time is required. In the event, however, that an extension of time is necessary to allow consideration of this paper, such an extension is hereby petitioned under 37 C.F.R. §1.136(a). Any additional fees believed to be due in connection with this paper may be charged to our Deposit Account No. 50-0220.

**Real Party In Interest**

The real party in interest is assignee SyneCor, LLC, of Durham, North Carolina.

**Related Appeals and Interferences**

Appellants are aware of no appeals or interferences that would be affected by the present appeal.

**Status of Claims**

Appellants appeal the final rejection of pending Claims 39-44 and 48-56 which, as of the filing date of this Brief, remain under consideration. The attached Claims

Appendix presents the claims at issue after entrance of Appellants' Amendment After Notice of Appeal filed on July 23, 2007.

**Status of Amendments**

The attached Claims Appendix presents the claims as amended by the Appellants in the Amendment After Notice of Appeal filed on July 23, 2007. As of the filing of this Brief, this Amendment has not been entered. However, as the Amendment After Notice of Appeal cancels Claims 27-34 and 38 and introduces no new issues, thereby simplifying the issues on appeal, Appellants believe this Amendment should be entered, and so will present this Brief as if the Amendment After Notice of Appeal has been entered.

**Summary of Claimed Subject Matter**

***Independent Claim 39***

Independent Claim 39 is directed to a method of producing a biocompatible stent for *in vivo* use, including:

providing a stent having a portion thereof formed from polymeric material selected from the group consisting of polylactic acid-polyethylene glycol block copolymer, poly(ethyleneoxide)-poly(butylenetetraphthalate), poly(lactic acid-*co*-lysine), a poly(L-lactic acid) copolymer and a poly( $\epsilon$ -caprolactone) copolymer, wherein the polymeric material contains one or more toxic materials;

immersing the polymeric material in a densified carbon dioxide composition such that the toxic materials are absorbed by the densified carbon dioxide composition, wherein pressure and/or temperature of the densified carbon dioxide composition is adjusted to selectively absorb toxic materials from the polymeric material;

removing the densified carbon dioxide composition containing the toxic materials from the polymeric material;

lowering the density of the removed densified carbon dioxide composition such that the toxic materials entrained therein become separated therefrom; and

removing the separated toxic materials, such that the stent is suitable for *in vivo* use.

The general method of Claim 39 is described, *e.g.*, in original Claim 15 of Appellants' application. The specific polymeric materials recited may be found, *e.g.*, on pages 9, lines 18-22 of Appellants' application. The recitation of a stent having a portion thereof formed from polymeric material may be found, *e.g.*, on page 7, lines 12 and 21-23 of Appellants' application.

***Independent Claim 40***

Independent Claim 40 is directed to a method of producing a biocompatible stent for *in vivo* use, including:

providing a stent having a portion thereof formed from polymeric material selected from the group consisting of: poly(lactic acid), poly(L-lactic acid), poly(D,L-lactic acid), and a copolymer of poly(lactic acid), poly(L-lactic acid), and/or poly(D,L-lactic acid), wherein the polymeric material contains one or more toxic materials;

immersing the polymeric material in a densified carbon dioxide composition such that the toxic materials are absorbed by the densified carbon dioxide composition, wherein pressure and/or temperature of the densified carbon dioxide composition is adjusted to selectively absorb toxic materials from the polymeric material;

removing the densified carbon dioxide composition containing the toxic materials from the polymeric material;

lowering the density of the removed densified carbon dioxide composition such that the toxic materials entrained therein become separated therefrom; and

removing the separated toxic materials, such that the stent is suitable for *in vivo* use.

The general method of Claim 40 is described, *e.g.*, in original Claim 15 of Appellants' application. The specific polymeric materials recited may be found, *e.g.*, on pages 9, lines 11-18 of Appellants' application. The recitation of a stent having a portion thereof formed from polymeric material may be found, *e.g.*, on page 7, lines 12 and 21-23 of Appellants' application.

***Independent Claim 50***

Independent Claim 50 is directed to a method of producing a biocompatible stent for *in vivo* use, including:

providing a stent having a portion thereof formed from polymeric material selected from the group consisting of: poly(glycolic acid), poly(D-lactic-co-glycolic acid), poly(L-lactic-co-glycolic acid), poly (D,L-lactic-co-glycolic acid), and a copolymer of poly(glycolic acid), poly(D-lactic-co-glycolic acid), poly(L-lactic-co-glycolic acid), or poly (D,L-lactic-co-glycolic acid), wherein the polymeric material contains one or more toxic materials;

immersing the polymeric material in a densified carbon dioxide composition such that the toxic materials are absorbed by the densified carbon dioxide composition, wherein pressure and/or temperature of the densified carbon dioxide composition is adjusted to selectively absorb toxic materials from the polymeric material;

removing the densified carbon dioxide composition containing the toxic materials from the polymeric material;

lowering the density of the removed densified carbon dioxide composition such that the toxic materials entrained therein become separated therefrom; and

removing the separated toxic materials, such that the stent is suitable for *in vivo* use.

The general method of Claim 50 is described, *e.g.*, in original Claim 15 of Appellants' application. The specific polymeric materials may be found, *e.g.*, on pages 9, lines 12-18 of Appellants' application. The recitation of a stent having a portion thereof formed from polymeric material may be found, *e.g.*, on page 7, lines 12 and 21-23 of Appellants' application.

**Grounds of Rejection to be Reviewed on Appeal**

Claims 39-44 and 48-56 stand rejected under 35 U.S.C. §102(e) as allegedly being anticipated by U.S. Patent No. 6,627,246 to Mehta et al. (hereinafter, referred to as "Mehta").

## Arguments

### **I. Introduction**

Under 35 U.S.C. §102, "a claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art reference." M.P.E.P. §2131 (quoting *Verdegaal Bros. v. Union Oil Co.*, 814 F.2d 628, 631, 2 U.S.P.Q.2d 1051, 1053 (Fed. Cir. 1987)). "Anticipation under 35 U.S.C. §102 requires the disclosure in a single piece of prior art of each and every limitation of a claimed invention." *Apple Computer Inc. v. Articulate Sys. Inc.*, 57 U.S.P.Q.2d 1057, 1061 (Fed. Cir. 2000). "The fact that a certain result or characteristic may occur or be present in the prior art is not sufficient to establish the inherency of that result or characteristic. To establish inherency, the extrinsic evidence 'must make clear that the missing descriptive matter is necessarily present in the thing described in the reference, and that it would be so recognized by persons of ordinary skill. Inherency, however, may not be established by probabilities or possibilities. The mere fact that a certain thing may result from a given set of circumstances is not sufficient.'" M.P.E.P. §2112 (citations omitted).

A finding of anticipation further requires that there must be no difference between the claimed invention and the disclosure of the cited reference as viewed by one of ordinary skill in the art. *See Scripps Clinic & Research Foundation v. Genentech Inc.*, 927 F.2d 1565, 1576, 18 U.S.P.Q.2d 1001, 1010 (Fed. Cir. 1991). In particular, the Court of Appeals for the Federal Circuit held that a finding of anticipation requires absolute identity for each and every element set forth in the claimed invention. *See Trintec Indus. Inc. v. Top-U.S.A. Corp.*, 63 U.S.P.Q.2d 1597 (Fed. Cir. 2002). Additionally, the cited prior art reference must be enabling, thereby placing the allegedly disclosed matter in the possession of the public. *In re Brown*, 329 F.2d 1006, 1011, 141 U.S.P.Q. 245, 249 (C.C.P.A. 1964). Thus, the prior art reference must adequately describe the claimed invention so that a person of ordinary skill in the art could make and use the invention.

### **II. The Final Action**

The Final Action cites Mehta as allegedly using a supercritical fluid (SCF) to extract solvent during the coating of a stent. *Final Action*, at pages 2-3, citing *Mehta* at col. 2, line 54 – col. 3, line 12; and col. 3, bottom – col. 4, top. Additionally, the Final Action

states that in Mehta, the process materials and coatings meet the instant language of the claims, “although the polymers are stated to be elastomerics, unusable in this process according to the declaration of 1/22/07.” *Final Action*, pages 2-3. The Final Action more specifically alleges that Mehta uses the same process, also coating stents with the same polymers, and using pressure and temperature to remove the solvents of the drugs and coatings. *Id.* at page 3.

### **III. Mehta**

At its broadest, Mehta describes deposition of a coating by altering the temperature and pressure of a SCF in which a drug or polymer to be coated is dissolved. *See Mehta*, col. 10, lines 31-33. Mehta specifically describes coating a stent with a polymer and/or a drug by using two different processes: (i) the Rapid Expansion of Supercritical Solutions, also referred to as RESS; and (ii) the Gas Anti-Solvent Process, also referred to as GAS (Mehta refers to the process as both GAS and GASS). *See Mehta*, col 10, line 31 through col. 12, line 67. Mehta also describes using a combination of the two processes to coat a stent with both a drug and a polymer. The RESS and GAS processes will be described in more detail below. *Id.*

#### *(a) Coating a Stent Using the RESS process*

To coat a stent using the RESS process, Mehta describes placing a stent into a pressurizable chamber along with a coating material (a drug and/or polymer). At this point, the coating material is not coated on the stent, but is contained within the same pressurizable chamber. Supercritical conditions are achieved such that the coating material becomes dissolved in the SCF. Once the system equilibrates, the chamber is rapidly depressurized, thus causing the coating material to precipitate from the SCF and form a coating on the stent. Thus, once the coating is formed on the stent, the stent is no longer immersed in a SCF. *See, e.g.*, col. 10, lines 33-45 and Example 1.

#### *(b) Coating a Stent Using the GAS process*

To coat a stent using the GAS process, Mehta describes dissolving a coating material (a drug and/or a polymer) in a liquid solvent to form a liquid solution. A stent is placed in the liquid solution, and the stent and liquid solution are contained within a

pressurizable chamber. As supercritical conditions are achieved in the chamber, the liquid solvent begins to dissolve in the SCF. However, the coating material is chosen to be insoluble in the SCF, so that as the liquid solvent dissolves in the SCF, which Mehta refers to as the SCF “extracting the solvent,” the coating material precipitates onto the stent, thereby forming the coating. *See, e.g.*, col. 10, line 64-col. 11, line 11 and Example 2.

#### **IV. Claims 39-44 and 48-56**

All of Claims 39-44 and 48-56 generally recite the steps of:

- (i) providing a stent having a portion thereof formed from polymeric material;
- (ii) immersing the polymeric material in a densified carbon dioxide composition such that the toxic materials are absorbed by the densified carbon dioxide composition;
- (iii) removing the densified carbon dioxide composition containing the toxic materials from the polymeric material;
- (iv) lowering the density of the removed densified carbon dioxide composition such that the toxic materials entrained therein become separated therefrom; and
- (v) removing the separated toxic materials, such that the stent is suitable for *in vivo* use.

It is important to note that, in the recited claims, the stent includes polymeric material *before* the immersion of the polymeric material in densified carbon dioxide. Although the claims do not limit the order of the steps in the recited processes, one of ordinary skill in the art would understand that the step of “providing” a stent would necessarily come before “immersing” the stent in carbon dioxide. To immerse a stent before providing it would be nonsensical.

Appellants further note that the recited claims refer to the removal of “toxic materials” from the polymeric materials. The methods of Claims 39-44 and 48-56 allow for stents to be formed using traditional polymer processing methods, which often include the use of toxic solvents, because the stents can be processed with carbon dioxide after formation to remove toxic residues without deforming the stent.

**V. Mehta Does Not Anticipate Claims 39-44 and 48-56**

Mehta does not anticipate Claims 39-44 and 48-56 for at least the reasons that Mehta does not describe the removal of toxic materials from polymeric materials included in a stent during its coating process; and Mehta does not describe providing a stent having a portion thereof formed from polymeric material, and immersing the polymeric material in a densified carbon dioxide composition such that the toxic materials are absorbed by the densified carbon dioxide composition.

**(i) *Mehta Does Not Describe the Removal of Toxic Materials From Polymeric Materials Included In a Stent***

The Final Action repeatedly refers to the extraction of the solvent in Mehta. *See Final Action*, pages 2-3. As such, Appellants assume the Final Action is equating the “solvent” of Mehta with the phrase “toxic materials” recited in the pending claims. However, upon close examination of Mehta, it can be seen that Mehta does not teach that solvent extracted during its process is toxic, and in fact, Mehta clearly states that its “process is environmentally friendly and does not require the use of toxic solvents.” Furthermore, in the examples, Mehta uses water as the solvent.

More specifically, Mehta describes two different types of solvents: (1) a SCF solvent (*see*, column 6, line 65 through column 7, line 55); and (2) a solvent for dissolving the polymer and/or drug (hereinafter, referred to as the “liquid solvent”), whereby the polymer and/or drug is precipitated by using a SCF anti-solvent via the GAS process. As the Final Action equates the SCF solvent with the densified carbon dioxide recited in the claims, and this solvent is nontoxic, Appellants believe the Examiner is equating the liquid solvent in Mehta with the toxic materials recited in the pending claims. However, Appellants note that Mehta does not provide *any* teaching that the liquid solvent is toxic, and in fact, teaches that its processes do not require the use of toxic solvents. Additionally, in the one example of the GAS process provided in Mehta, the liquid solvent is water.

Therefore, Appellants submit that Mehta does not teach or suggest using carbon dioxide to absorb toxic materials from polymeric material included in a stent. As such, Mehta does not teach each and every element of Claims 39-44 and 48-56, and so Mehta does not anticipate Claims 39-44 and 48-56.

**(ii) Mehta Does Not Describe Absorbing Toxic Materials From A Stent Having A Portion Thereof Formed From Polymeric Material**

Appellants further submit that even assuming *arguendo* that the liquid solvent in Mehta could be toxic, Mehta would still not anticipate Claims 39-44 and 48-56 because Mehta does not describe the steps of (i) providing a stent having a portion thereof formed from polymeric material that contains one or more toxic materials and (ii) immersing the polymeric material in a densified carbon dioxide composition such that the toxic materials are absorbed by the densified carbon dioxide.

Stated another way, Mehta is a coating process using SCF to deposit the polymer, either via precipitation of the coating material from the SCF, or via precipitation of the coating material from a liquid solvent, by using a SCF anti-solvent. In Mehta, the polymeric material from which the solvent is allegedly extracted is not present until *after* the stent is immersed in the SCF. In contrast, in the instant claims, the stent has a portion formed from polymeric material prior to immersion in carbon dioxide. As stated above, although Claims 39-44 and 48-56 do not limit the order of the steps in the recited processes, one of ordinary skill in the art would understand that the step of providing a stent would necessarily come before immersing the same stent in carbon dioxide. Therefore, Mehta does not include the element of the claims whereby a stent having a portion thereof formed from polymeric material is provided and then immersed in densified carbon dioxide such that toxic materials in the polymeric material (of the stent) are absorbed by the densified carbon dioxide.

Appellants note that although the stents of Mehta may be formed of polymeric material, this is not the polymeric material that is described as having solvent extracted therefrom. Even for polymer-containing stents, Mehta describes the solvent as being extracted from the polymeric material that is coated onto the stents during a GAS process, *not* from the polymeric material present prior to immersion of the stent.

Therefore, for this additional reason, Appellants submit that Mehta does not teach each and every element of Claims 39-44 and 48-56, and so Mehta does not anticipate Claims 39-44 and 48-56.

**VI. Mehta Describes the Use of Thermoplastic Elastomers**

As discussed above, the Final Action states that in Mehta, the process materials and coatings meet the instant language of the claims, “although the polymers are

stated to be elastomerics, unusable in this process according to the declaration of 1/22/07.” *Final Action*, pages 2-3. Appellants believe this assertion is incorrect, and so will briefly address it below.

The Declaration of inventor Dr. Joseph DeSimone, submitted on January 24, 2007 (hereinafter, the “DeSimone declaration”), states that the recited polymeric materials are thermoplastic, while the Bawa et al. reference (U.S. Patent No. 6,071,439, previously cited during prosecution) describes the use of crosslinked elastomers. The DeSimone declaration does not state that the instant processes cannot be used on stents that include elastomers. The DeSimone declaration states that “a polymer chemist or engineer would not have expected that the methods of Bawa et al., which related to the treatment of crosslinked elastomers, could be used on a stent formed from thermoplastic materials without deforming the stent.” *DeSimone Declaration*, para. 10. Thus, the DeSimone declaration and Appellants response dated January 24, 2007 are directed to establishing the non-obviousness of the pending claims over Bawa et al., and do not assert that elastomeric polymers are unusable in the instant processes.

Furthermore, Appellants emphasize that the DeSimone declaration highlighted the difference between thermoplastic polymers and crosslinked elastomers. Mehta describes some of its copolymers as being elastomeric, whereby some of the materials are the same as those recited in the pending claims. However, none of the Mehta’s stated elastomeric copolymers are crosslinked. Therefore, these polymers fall into the class of thermoplastic elastomers. Appellants submit herewith (*see* Evidence Appendix), a portion of the text “Polymer Science and Technology,” (Joel R. Fried, Prentice Hall Professional Technical Reference, 2003, pages 377-378) which describes how certain uncrosslinked materials can be both thermoplastic and elastomeric. Therefore, Mehta’s teaching that specific materials (*see*, columns 5 and 6) may be elastomeric is not in conflict with the DeSimone declaration.

**Conclusion**

In light of the above discussion, Appellants submit that each of the pending claims is patentable over the cited references and, therefore, request reversal of the rejections of Claims 39-44 and 48-56.

Respectfully submitted,



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Anthony DeRosa

**CLAIMS APPENDIX**  
**Pending Claims Serial No.: 10/662,621**  
**Filed: September 15, 2003**

39. (Previously Presented) A method of producing a biocompatible stent for *in vivo* use, comprising:

providing a stent having a portion thereof formed from polymeric material selected from the group consisting of polylactic acid-polyethylene glycol block copolymer, poly(ethyleneoxide)-poly(butylenetetraphthalate), poly(lactic acid-*co*-lysine), a poly(L-lactic acid) copolymer and a poly( $\epsilon$ -caprolactone) copolymer, wherein the polymeric material contains one or more toxic materials;

immersing the polymeric material in a densified carbon dioxide composition such that the toxic materials are absorbed by the densified carbon dioxide composition, wherein pressure and/or temperature of the densified carbon dioxide composition is adjusted to selectively absorb toxic materials from the polymeric material;

removing the densified carbon dioxide composition containing the toxic materials from the polymeric material;

lowering the density of the removed densified carbon dioxide composition such that the toxic materials entrained therein become separated therefrom; and

removing the separated toxic materials, such that the stent is suitable for *in vivo* use.

40. (Previously Presented) A method of producing a biocompatible stent for *in vivo* use, comprising:

providing a stent having a portion thereof formed from polymeric material selected from the group consisting of: poly(lactic acid), poly(L-lactic acid), poly(D,L-lactic acid), and a copolymer of poly(lactic acid), poly(L-lactic acid), and/or poly(D,L-lactic acid), wherein the polymeric material contains one or more toxic materials;

immersing the polymeric material in a densified carbon dioxide composition such that the toxic materials are absorbed by the densified carbon dioxide composition, wherein pressure and/or temperature of the densified carbon dioxide composition is adjusted to selectively absorb toxic materials from the polymeric material;

removing the densified carbon dioxide composition containing the toxic materials from the polymeric material;

lowering the density of the removed densified carbon dioxide composition such that the toxic materials entrained therein become separated therefrom; and

removing the separated toxic materials, such that the stent is suitable for *in vivo* use.

41. (Previously Presented) The method of Claim 40, wherein the one or more toxic materials are selected from the group consisting of organic solvents (polar or non-polar), unpolymerized monomers, polymerization catalysts, oligomers, and polymerization initiators.

42. (Previously Presented) The method of Claim 40, wherein the densified carbon dioxide composition is a liquid composition, and wherein the immersing and removing steps are carried out in an enclosed chamber.

43. (Previously Presented) The method of Claim 40, wherein the step of lowering the density comprises reducing pressure and/or increasing temperature of the densified carbon dioxide composition.

44. (Previously Presented) The method of Claim 40, wherein carbon dioxide in the densified carbon dioxide composition is present in a supercritical state.

45-47. (Cancelled).

48. (Previously Presented) The method of Claim 40, wherein the carbon dioxide contains one or more of a co-solvent, a surfactant, and a co-surfactant.

49. (Previously Presented) The method of Claim 40, wherein the polymeric material is a coating on one or more portions of the stent.

50. (Previously Presented) A method of producing a biocompatible stent for *in vivo* use, comprising:

providing a stent having a portion thereof formed from polymeric material selected from the group consisting of: poly(glycolic acid), poly(D-lactic-co-glycolic acid), poly(L-lactic-co-glycolic acid), poly (D,L-lactic-co-glycolic acid), and a copolymer of poly(glycolic acid), poly(D-lactic-co-glycolic acid), poly(L-lactic-co-glycolic acid), or poly (D,L-lactic-co-glycolic acid), wherein the polymeric material contains one or more toxic materials;

immersing the polymeric material in a densified carbon dioxide composition such that the toxic materials are absorbed by the densified carbon dioxide composition, wherein pressure and/or temperature of the densified carbon dioxide composition is adjusted to selectively absorb toxic materials from the polymeric material;

removing the densified carbon dioxide composition containing the toxic materials from the polymeric material;

lowering the density of the removed densified carbon dioxide composition such that the toxic materials entrained therein become separated therefrom; and

removing the separated toxic materials, such that the stent is suitable for *in vivo* use.

51. (Previously Presented) The method of Claim 50, wherein the one or more toxic materials are selected from the group consisting of organic solvents (polar or non-polar), unpolymerized monomers, polymerization catalysts, oligomers, and polymerization initiators.

52. (Previously Presented) The method of Claim 50, wherein the densified carbon dioxide composition is a liquid composition, and wherein the immersing and removing steps are carried out in an enclosed chamber.

53. (Previously Presented) The method of Claim 50, wherein the step of lowering the density comprises reducing pressure and/or increasing temperature of the densified carbon dioxide composition.

54. (Previously Presented) The method of Claim 50, wherein carbon dioxide in the densified carbon dioxide composition is present in a supercritical state.

55. (Previously Presented) The method of Claim 50, wherein the carbon dioxide contains one or more of a co-solvent, a surfactant, and a co-surfactant.

56. (Previously Presented) The method of Claim 50, wherein the polymeric material is a coating on one or more portions of the stent.

**EVIDENCE APPENDIX**  
**Serial No.: 10/662,621**  
**Filed: September 15, 2003**

Joel R. Fried, *Polymer Science and Technology*, 2003, Prentice Hall Professional Technical Reference, Upper Saddle River, NJ, pages 377-378.

**RELATED PROCEEDINGS APPENDIX**  
**Serial No.: 10/662,621**  
**Filed: September 15, 2003**

None.

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Second Edition

Joel R. Fried

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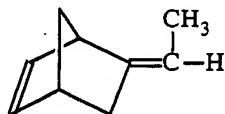
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ter segments, which phase whose  $T_g$  is seen urethane groups physical anchor sites stretched. When the stallize until tension strength, chemical resis- stable to attack by and oxygenated sol- n'garments, surgical

NH—Ar—N=C=O

O<sub>n</sub>O<sub>n</sub>

applications.

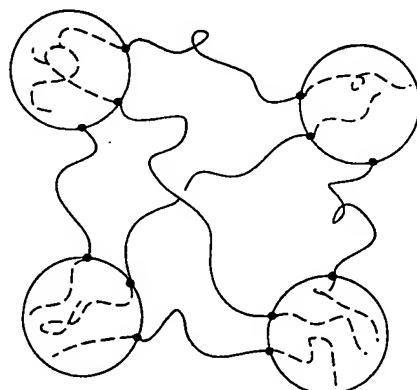
ethylene and propylene (see Section 2.2.3) at placement of monomer crosslinked with perox- a. Alternately, an un- propylene, and unconju- ethylidene norbornene

These unsaturated terpolymers may be vulcanized by traditional means. EPM and EPDM have good resistance to acids, good weatherability and color stability, and good electrical stability. They can be used as substitutes for SBR and neoprene in automotive applications such as in tires, radiator hose, gaskets, and seals. EPM and EPDM are also used in wire and cable insulation, weather stripping, and in footwear. Blends of polypropylene and EPDM are used as material in the manufacture of car bumpers.

### 9.2.3 Thermoplastic Elastomers

Commercial elastomers can be made without the formation of the permanent crosslinks that are normally created through vulcanization. In place of covalent bonds, rigid-domain structures are used to create a network structure, as illustrated in Figure 9-9. These are typically the crystalline or glassy phases associated with the crystalline or glassy blocks of block copolymers or result from associations formed through the creation of secondary bonds such as hydrogen bonding between chemical groups in different molecules. Since these domains are physical in nature, they are normally reversible and therefore elastomers belonging to this class are thermoplastic and can be fabricated by conventional molding techniques. Thermoplastic elastomers can be made from polyurethanes (discussed in Section 9.2.1), polyesters, polyolefins, and styrenic block copolymers. The absence of a separate vulcanization step and easy recycling of these materials have led to rapid commercialization of thermoplastic elastomer over the past 30 years.

**SBS Elastomers.** The most commercially important thermoplastic elastomers are ABA block copolymers composed of a high-molecular-weight (50,000 to 100,000) polystyrene end block and a central block of low-molecular-weight (10,000 to 20,000) polybutadiene (YSBR) or other olefins such as isoprene and ethylene-butylene. When cooled from the melt to below their glass-transition temperature, the PS-blocks phase separate to form rigid glassy domains that act as physical crosslinks for the elastomeric olefin blocks. These block copolymers are prepared by anionic "living" polymerization as discussed in Section 2.2.2. As a class, they have higher tensile strength than SBR rubber but have limited heat resistance. YSBR can be hydrogenated to improve weather and temperature resistance. Blends of styrenic thermoplastic elastomers are used in rubber bands, toy products, shoe soles, and gasket material. YSBR containing 30% polybutadiene content may be blended with PS to produce a resin suitable for thermoforming plastic drinking cups. PS alone is too brittle to withstand the high extension resulting from thermoforming (see Section 11.1.2).



**Figure 9-9** Representation of glassy domains in a thermoplastic elastomer such as SBS, polystyrene-*block*-polybutadiene-*block*-polystyrene. Circles represent physically separated domains of high glassy polymer (e.g., polystyrene) content that serve as physical crosslinks. Glassy domains are interconnected by the elastomeric (e.g., polybutadiene) segments. (Adapted from L. H. Sperling, *Introduction to Physical Polymer Science*. Copyright ©1986 John Wiley & Sons. This material is used by permission of John Wiley & Sons, Inc.)

**Olefinic Elastomers.** Olefinic thermoplastic elastomers, prepared by use of Ziegler–Natta catalysts (see Section 2.2.3), include *polyallomers*, which are block copolymers of polypropylene (the hard, crystalline block) and a second olefinic block, usually ethylene or ethylene and a diene (EPDM). EPDM block copolymers are attractive replacements for neoprene in oil-resistant wire and cable insulation due to their superior processability and coloration properties.

**Copolyesters.** Thermoplastic copolymers consist of a hard (crystalline) polyester block, such as that formed by the reaction of terephthalic acid and butanediol, and a soft block of an amorphous long-chain polyester (e.g., polytetramethylene ether glycol) soft block. Like thermoplastic polyurethanes, thermoplastic copolymers have good hydrocarbon and abrasion resistance. Applications include wire and cable insulation, gaskets, seals, hose, and automotive parts.

## 9.3 THERMOSETS

Principal commercial thermosets include epoxies, polyesters, and formaldehyde-based resins (i.e., phenol-formaldehyde, urea-formaldehyde, and melamine-formaldehyde). As shown by data given in Table 9-8, phenol resins constitute the largest segment of the thermoset market that represents approximately 12% of the total U.S. plastics production.

Table 9-8 U.S. Thermosets

Thermosets
Phenol resins
Urea resins
Polyesters (unsaturated)
Epoxies
Melamine resins

<sup>\*</sup>Chemical and Engineering News

<sup>†</sup>Recent data incomplete  
News, June 24, 2002.

### 9.3.1 Epoxies

Epoxies are formed by a two-step reaction. The first step is the reaction of epichlorohydrin with a base-catalyzed by triethylamine (NEt<sub>3</sub>) to form epichlorohydrin. The second step is the reaction of epichlorohydrin with a nucleophile, such as a phenol or amines, to form epoxides. The epoxide group is a three-membered ring containing one carbon atom and two oxygen atoms. The epoxide group is highly reactive and can react with a variety of nucleophiles to form a wide range of epoxy resins.

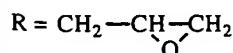
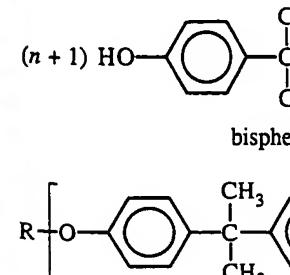


Figure 9-10 Epoxy